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NAME AND ADDRESS DATE

ON ABIETIC ACID and RELATED RESIN ACIDS
from OLEORESIN of AMERICAN CONIFERS

By

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Table of Contents.

Abietic acid from American rosin.
- Preparation of abietic acid according to Flueckiger's method.
- Double decomposition between lead abietate and organic halides.

The resin acids from the Digger's pine.
- The separation of the oleoresin into volatile oil and resin.
- Fractional precipitation of the resin acids in the form of theie lead salts.
- Regeneration of the resin acid from the lead salt by means of
  - 1.)Hydrogen sulphide
  - 2.)Sulphuric acid
  - 3.)Hydrogen chloride.(Isolation of crystalline resin acid)
- Distillation of resin under diminished pressure and preparation of crystalline resin acid.

The resin acids from Canada balsam.
- History of Canada balsam.
- Physical constants of Canada balsam.
- Chemical constants of Canada balsam.
- Chemical examination of Canada balsam.

Volatile oil

Resin

The resin acids from Oregon balsam.

Preliminary examination of an oleoresin from Douglas fir.

Bibliography.

I. ABIETIC ACID FROM AMERICAN ROSIN

Preparation of Abietic Acid According to Flückiger's Method

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Ten kilograms of commercial rosin were obtained from the storeroom and broken into small lumps so as to be conveniently handled. The rosin was then placed in suitable flasks and treated with 70 p. c. alcohol according to the method followed by Flückiger.(1)

The first solid material that settled out from the alcoholic solution of rosing was separated by filtering and subsequently dissolved in 95 per cent alcohol. This solution was then allowed to evaporate slowly in a crystallizing dish. The solid that crystallized out was separated by the force filter, dissolved in hot alcohol and re-crystallized. The acid obtained was put into a bottle. From time to time the alcoholic solution of rosin was heated on a water bath, the alcoholic vapor being condensed by means of a reflux condenser. After a few weeks more of the impure abietic acid settled out of

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(1) Journ. f. prackt. Chemie., 101,(1867) p. 235.

the solution. The solid material was separated in every case by filtration followed by gently washing the acid with a small amount of alcohol, then re-crystallizing the acid from 95 per cent alcohol.

By successive crystallizations extending over a period of three months about 200 grams of resin acid were obtained in fairly pure condition. This was placed in a glass stoppered bottle and labeled Material "A".

During the first crystallization from alcohol only the purer acid was re-dissolved. The impure solid was set aside in each case and finally mixed with that obtained from the acetic acid crystallization which see.

Approximately 200 grams of equally pure abietic acid were contaminated with copper when the flask containing the alcoholic solution of the acid broke and the contents ran into a copper water bath. As much of the material as could be saved was dried and placed into a flask. This was labeled material "B".

The alcoholic filtrates, left after filtering off the pure abietic acid, were placed in a large jar and allowed to stand for several weeks. During this time very little acid separated. By the addition of a few cubic centimeters of hydrochloric acid at the suggestion of Mr. Ellingston about one pound of acid settled out in less than a week. The alcoholic filtrate was placed in a separate glass jar and labeled material "C".

The solid material separated by filtering was dissolved with alcohol, but turned a deep brown color. The solid material crystallizing out was taken up with acetic acid. The alcoholic filtrate obtained by the last filtration was mixed with the acetic acid filtrated and the resulting mixture was set aside for one month. The acid separating out in this time was dissolved in acetic acid and recrystallized. The impure acid so obtained was dried, put in a glass bottle labeled material "D".

The yield of impure abietic acid in this separation together with the impure acid that was set aside from the former alcoholic crystallizations amount to approximately 800 grams. The mother liquor obtained in this case was put in a glass bottle and labeled material "E".

Approximately 10 per cent of the original rosin was recovered as resin acids, varying in quality from the transparent triangular crystals of the fairly pure acid to the yellow substance obtained in the last separation.

Double Decomposition Between
Lead Abietate and Organic Halides

Approximately fifty grams of the pure resin acid were ground to a fine powder and mixed with strong alcohol. To this part was added some (1) alcoholic lead subacetate.

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(1) Not enough lead acetate acid had been added, hence product "A" is presumably a mixture of lead abietate and abietic acid.

The solid material was allowed to settle and then separated, dried and set aside for further use. Labeled material "A".

This lead salt was prepared with the intention of treating it with the halides of hexane, heptane and allied esters. Shortness of time prevented any experiments being worked out in this connection.

Six grams of abietic acid were obtained from Mr. Ellingston for some preliminary work. The acid was thoroughly powdered, dissolved in alcohol and lead acetate added. The precipitate after settling was dried and set aside.

Dicarvacrol Diiodide

Two grams of lead abietate were placed in a test tube and to this was added a few ccm. of alcohol. One gram of dicarvacrol diiodide was shaken up with the alcoholic mixture. After heating with the reflux condenxer for one-half hour, the mixture apparently contained unchanged lead abietate as well as lead iodide.

Hexyl iodide

Equal volumes of lead abietate and hexyl iodide were put in a flask and heated under a reflux condenser one half hour. A yellowish precipitate settled out, this was filtered off, mixed with more lead abietate and refluxed one-half hour more. A yellowish powder settled out. This was separated by filtering. The two filtrates so far obtained were placed in a small beaker and allowed to evapor-

ate slowly. The resin left upon evaporation had the appearance of a thickened varnish and was of a brownish color.

Approximately one gram each of the acetates of copper, cadmium, calcium, silver and zinc was put into separate flasks and 10-15 ccm. of alcohol added. Heat was applied until a saturated solution of the salt was obtained. The undissolved portion was filtered off and thrown away. The alcoholic solutions were put in separate test tubes and about one-half a gram of lead abietate was added to each one. The mixture was allowed to stand several hours.

In the case of the cadmium acetate a precipitate was produced, copper acetate gave a heavy precipitate also. Calcium acetate gave only a slight cloudiness. In the case of the silver salt there was a suspicion of a precipitate. The zinc salt gave a clear white precipitate.

II. RESIN ACIDS FROM DIGGERS PINE

Separation of the Oleoresin into Volatile Oil & Resin

The method used was the same as employed for the general examination of all oleoresins. 500 grams of the crude resin were distilled with steam in a tared 1.5 liter balloon flask, with a Kjeldahl connecting bulb tube placed between the flask and condenser to prevent any rosin from being carried over mechanically. The rosin left in the flask was kept heated until all the water had been expelled,

care being taken that the temperature did not exceed 145°. When bubbles ceased to form on the surface of the rosin, on agitation, the removal of the water was considered complete. The rosin was then strained through two layers of fine muslin, and that which adhered was completely removed by extraction with chloroform. The volatile oil was separated from the water and carefully dried.

Fractional Precipitation of the Resin Acids in the Form of Their Lead Salts

Another portion of resin from Diggers pine was dissolved in alcohol, filtered, and placed in a large wide mouthed bottle. Six fractional precipitates of the lead salt were made by adding lead acetate (alcoholic). After the sixth addition of lead acetate and the removal of the corresponding precipitate no more lead salt was thrown down by the addition of lead acetate.

The fractional precipitates were properly labeled and the metallic lead determined as lead oxide, was quantitatively formed in each case.

	Per cent as PbO.				
	I.		II.		
Precipitate No. I	4.90	p.c.	4.82	p.c.	"B"
Precipitate No. II	10.81	"	10.74	"	"C"
Precipitate No. III	14.55	"	14.64	"	"D"
Precipitate No. IV	18.45	"	18.40	"	"E"
Precipitate No. V	19.32	"	19.28	"	"F"
Precipitate No. VI	20.56	"	20.51	"	"G"

The filtrate from the lead acetate precipitation was treated as follows: Fractional precipitates were obtained (H.I.J.K.L.) by adding lead sub-acetate until no further sub-acetate was obtained and then the mother liquor was set aside in a cool place and left several weeks. Gradually a white crystalline solid was found deposited upon the sides of the bottle. ("M"). Upon a quantitative determination of the lead as oxide in the compound so formed it was found to be 52.3% PbO. This is approximately the same as the theoretical percentage of lead oxide corresponding to the sub-abietate. $(C_{20}H_{27}O_2)_2$ PbO.

Regeneration of the Resin Acid from the Lead Salt by means of:

The lead salt obtained from the sixth precipitation ("G") with alcoholic lead acetate was used to secure a resin acid.

I. Hydrogen Sulphide.

An attempt to regenerate the acid by precipitating the lead as sulphide from the alcoholic mixture gave only amorphous products.

II. Sulphuric Acid.

100 grams of the lead precipitate (No. 6) were treated with double the amount of sulphuric acid as ethyl sulphate necessary to precipitate the lead in the sample. The mixture was stirred and allowed to stand over night. The solution was filtered and the precipitate thrown away.

The filtrate after standing several days did not give any crystals.

III. Hydrogen Chloride.

Another 100 grams of lead precipitate were treated with a hydrochloric acid solution of alcohol. An equivalent quantity of this solution was added to the lead salt. The precipitate was filtered off and the filtrate was set aside and allowed to evaporate slowly. After about two weeks crystals were observed in the mother liquor. The syrupy liquid surrounding the crystals was removed by washing with a mixture of acetic acid and acetone. The resin acid was taken purified by re-crystallizing from pure acetone.

The melting point was found to be between 145-150°C., after the third crystallization.

Several solvents were used for the purification of the resin acid. The following were used: Acetone, amyl alcohol, ethyl alcohol, methyl alcohol, ether, chloroform, ethyl acetate and acetic acid. All but the acetone proved to be unsatisfactory for the separation of the mother liquor from the resin acid.

Distillation of Resin under Diminished Pressure and Preparation of Crystalline Resin Acid

The experiment for obtaining a resin acid by means of diminished pressure was carried out successfully by using the resin and oleoresin in a similar manner. The

resin was dissolved in alcohol and the solution was then filtered. The resin obtained after the evaporation of the alcohol was clear and quite hard. The oleoresin was not previously heated but distilled as it came from the trees.

100 grams of material were used in each experiment. The distillation was carried on in an ordinary round bottom distilling flask. The distillate started to come over at a temperature of about 220°. In the case of the resin, the maximum temperature was reached at 240°, while the oleoresin could be distilled to 260° without any decomposition. The pressure in both cases was kept fairly constant at 18-20 mm.

The distillate upon cooling became very hard in both cases. That obtained from the resin was taken up with acetone and slowly allowed to evaporate. In a few days crystals were observed in the mother liquor. The supernatant liquid was removed by alcohol and after drying, the resin acid on the force filter, it was re-crystallized from pure acetone. The melting point in both resin acids was found to be 152°-155° C. Labeled "A".

III. THE RESIN ACIDS FROM CANADA BALSAM

History of Canada Balsam

It has been assumed that the Canadian Indians were acquainted with the exudation commonly called Canada

balsam,(1) and that the French, in whose possession Canada remained until the year 1763 "were probably acquainted with Canada balsam long before this period."(2) Indeed we are informed that specific references to this balsam are found in the "Histoire de la Nouvelle-France" by Marc Lescarbot, who traveled in Canada in the years 1606 and 1607.(3) However, a careful scrutiny of the statements of Lescarbot referred to, do not reveal that such is necessarily the case. Moreover, a careful perusal of the available literature pertaining to Hebert,(4) apothecary and first permanent settler of Canada, and of Giffard, surgeon and in a measure a successor to Hebert as medical advisor of the colony, do not reveal that these men had any knowledge of Canada balsam. Such being the case, we are not surprised that whereas the references to firs in the accounts sent by the Jesuit missionaries to their superiors are

(1) Gildemeister und Hoffmann, Die aeth. Oele, 2nd. ed., p. 105.

(2) Flueckiger, Pharmacographia, p. 612.

(3) Tschirch and Bruening, Arch. der Pharm. 238, p. 488
(3) See also Gildemeister, k. c. p. 105.

(4) See Bibliography: Lescarbot, 1612.

numerous,(1) none of them bear on the subject of the balsam itself.

The first known statement that can be construed with reasonable probability as applying to Canada balsam appears to have been made by Boucher(2) in his History of New France first published in 1663.

When we learn that Canada balsam was a "current article of pharmacy" in Strassburg as early as 1759, we are suprised to learn that it is not mentioned by Peter Kalm who toured New France as well as the British colonies during 1748-49. At least Fr. Hoffmann who reviewed the pharmaceutical aspects of the report of this naturalist(4) makes no mention of it. This is all the more remarkable, since Kalm enjoyed the company of Dr. Gaulthier(5) while in Quebec and the surrounding country. He did, however, take notice of the pitch kilns at the Bay of St. Paul.(6)

New France being a French colony, we naturally would seek for the earliest references to Canada balsam in the pharmaceutical treatises by French authors. Yet as Fluckiger(7) points out, no mention of it is found in

(1) See index volume to the seventy-one volumes of Thwaites' Jesuit Relations.
(2) See Bibliography: Boucher, 1664.
(3) Fragmentary notes from the reports of two early naturalists on North America. PH. Rev. 16. p. 260.
(4) Pharm. Rev., 11, p.
(5)
(6) Ph. Rev., 11, p. 264.
(7) Pharmacographia P. 612; also Tschirch, Archiv d. Pharm. 238, p. 488.

Pomet's History of Drugs, editions of 1694 and 1735.(1) The same student of history of drugs points out that only a few years later Lemery includes it in the third edition of his Universal Dictionary of simple drugs(1748)(2) under the designation "Baum de Canada", and that this Parisian apothecary and physician recommended it for internal use. Flueckiger adds that "in 1759 it was at Strassburg a current article of pharmacy".(3) Tschirch(4) thinks it strange that Canada balsam should be found in a medical price list of Strassburg when it was not generally known in London. It should be remembered, however, that in 1759 Strassburg was a French city and, no doubt, in closer touch with the French colonies and French pharmaceutical progress then London.

Canada having become an English colony in 1763, it is of interest to note that under the title of "Balsamum Canadense", Canada balsam occurs in the Materia Medica list of the London Pharmacopoeia of 1788;(5) also that the books of the London druggist, J. Gurney Bevan, reveal that its wholesale price in 1776 was 4s., in 1788, 5s., per lb.(6) Tschirch quotes the price "4 shillings" per "Lot",

(1) Histoire gènèrale des drogues. 1694 and ibidem 1735.
(2) Pharmacognosie, 3d ed., p. 81.
Dictionaire Universal des drogues simples. 3d ed. Paris 1748.
(3) Pharmacographia, p. 612, Pharm. Journ., 35, p. 1021; Documents zur Geschicte der Pharmacie, Halle, 1876, p. 961 reprinted from the Archiv. der Pharmacie, vols., 207 7 208.
(4) Arch. d. Pharm., 238 p. 488.
(5) See bibliography: Pharmacopoeia Londinensis

i.e., per 1/2 ounce.(1) Apparently this is due to a typographical error. However, even before Canada became an English colony, and before Canada balsam became an article of the London drug market, it appears to have attracted the attention of English authors of materia medica. Thus Lewis, in his History of Materia Medica of 1761 makes mention of it.

In as much as the early physicians of the thirteen colonies and of the newly organized United States of America resorted largely to the use of imported drugs and according to Schoeff neglected their "rich domestic materia medica"(2) we are not surprised that Canada balsam appears to have become know later in this country than in Europe. However, whereas Kalm(3) does not appear to mention it in the account of his travels, 1748-49, nor Schoeff in the account of his travels, 1783-84, the latter naturalist and physician enumerates it in his "American Materia Medica, principally of the vegetable kingdom"(4) published in Erlangen in 1787.

In his "Account of some of the vegetable productions naturally growing in this part of America" presented to the Am. Acad. of Arts and Sciences in 1785,

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(1) Archiv. der Pharmacie, 238, p. 488.
(2) Ph. Rev. 16, p. 298.
(3) Fr. Hoffman in his "Fragmentary notes from the reports of two early naturalists on North America", while looking specially for this sort of information, does not mention it. Ph. Rev., 16, p. 296.
(4) See Bibliography: Schoeff, 1877.

Manasseh Cutler enumerates "The fir" (p. 490)(1) under the genus "Pinus" but records not a word as to its natural history or uses.

To infer from this that Canada balsam was well known in the United States at that time, might, however, be misleading. Barton, in his Collections for an essay towards a materia medica of the United States, of which the first part was published in 1798, the second part in 1804, does not mention it. Not that he was not acquainted with Schoepf's compilation, for he refers to it with some praise (p.2), but he also accuses Schoepf of having been too credulous (p.3) and of ascribing "powers to plants which are merely inert" (p.3).(2) Apparently he did not regard Canada balsam as worth mentioning in his list of American drugs. While Barton might be regarded as one of the more conservative of the reactionaries against the old school of American practitioners, Peter Smith certainly is a liberal among the unorthodox. Yet he also makes no mention of Canada balsam in "The Indian Doctor's Dispensatory".(3)

(1) See Bibliography.
(2) Page reference No. 7 of Bulletin of the Lloyd Library. 1903. These page references are also to the reprint which appeared as No. 1 of the Bulletin of the Lloyd Library in 1900.
(3) Reprinted as No. 2 of the Bulletin of the Lloyd Library, 1901.

Physical Constants of Canada Balsam

The only physical constants that have been recorded pertain to the specific gravity, direction and degree of rotation, and solubility of the balsam. For the purpose of enableing a better oversight, the constants recorded are herewith tabulated.

Specific Gravity.

Date	Observer	Sp. Gr.	Remarks
1879	Flueckiger	0.998 at 14.5°	

Neither the 1880 nor the 1890 editions of the U. S. P. in which Canada balsam was official as Terebinthina Canadensis, give the specific gravity of the oleoresin in either definition or descriptive part of the text. It was not official in any of the foreign pharmacopoeias included in the compilation of the second edition of Hirsch's Universalpharmakopoe of 1902. Neither Thirch(1) nor Dieterich(2) quote the specific gravity of Canada balsam. Hence it would seem that the specific gravity is not regarded as a criterion of any importance in the examination of this natural product.

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(1) Die Harze.

(2) Analysis of resins, balsams and gum-resins.

Chemical Constants

It is only in recent years that some of the chemical constants of Canada balsam have been determined in accordance with the general methods of investigation of oleoresins, balsams and resins. All of these determinations, however, have been made, not with authentic material, but on commercial products.

Acid, Ester and Saponification Values

Observer	Acid Value direct (S.-Z.d)	Ester Value (E.-Z.)	Sap. Value hot (V.-Z.h)
A. Kremel(1) I	83.0		
" II	81.3		
F. Dietze(2) I	84.89	4.54	89.43
" II	85.93	9.83	95.76
" III	84.40	9.00	93.40
E. Dieterich(3)	84.0 to 86.8		

Optical Rotation

Kradwell(4) appears to have been the first and only observer thus far to determine the angle of rotation of the oleoresin. He found that "the balsam deviates the plane of polarized light about five degrees to the right".

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(1) Notizen zur Pruefung der Arzneimittel (1889, p. through Dieterich-Salter, Analysis of resins, p.60.

(2) Suedd. Apt. Ztg. (1897) No. 44, p. through D-S., Analysis, p. 61.

(3) Decennium der Helfen ber ger Annolen, p.

(4) Proc. W. P. A., 12, p. 39.

Solubility

U. S. Pharm. p. 451, 1900 edition -- "completely soluble in chloroform, benzene and ether.

Iodine Value

The following iodine values were obtained by Dieterich,(1) viz., but they are admittedly of no value.

Methoxyl Value

Greger and Bomberzer(2) found the methoxyl value to equal 0.

Chemical Examination

The first chemical investigation of Canada balsam was apparently made by Bonastre in 1825. The oleoresin as a whole, or its components the resin and volatile oil were further examined in 1827 by Unverdorben, in 1830 by Cailliot, in 1849 by Wirzen, in 1891 by Dradwell, also by Kressin, in 1879 by Flueckiger, in 1892 by Emmerich, in 1894 by Hunkel, in 1900 by Tschirch and Bruening. Brief statements as to the results obtained by these investigators will be found in the bibliography.

The sum total of these investigations is rather

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(1)

(2)

meagre. So far as the volatile constituents are concerned the presence of pinene was surmised by Flueckiger. The presence of l-pinene was definitely established by Kradwell, Kressin, Emmerich and Hunkel. That of l-bornyl acetate by Hunkel. As to the non-volatile constituents Caillot reports on a crystalline "abietine", whereas Flueckiger points out the absence of any crystalline resin, but Kradwell in 1891 observed "a crystalline substance, which will very likely prove an acid". Tschirch and Bruening obtain 0.3 p. c. of a crystalline acid $C_{19}H_{28}O_2$ which they name canadolic acid. All other constituents reported upon are amorphous. Tschirch and Bruening(1) who in 1900 distilled the oil, point out that whereas the freshly distilled oil has an odor reminding one of balm and lemon, upon standing the terebinthinate odor develops and predominates. No chemical study of the oil appears to have been made by them.

Volatile Oil

The oil from several commercial samples of Canada balsam being available, it was subjected to a somewhat careful fractionation for the purpose of throwing more light, if possible, upon its composition. The

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(1) Arch. d. Pharm., 238, p. 503.

several oils were first subjected to steam distillation with the aid of a Geer's column in order to ascertain how these oils compared with ordinary turpentine oils. The results are herewith tabulated separately:

1.) For the oil from the balsam obtained from McKesson & Robbins.

2.) For the oil from the balsam obtained from the Milwaukee Drug Co.

3.) From the remnants left from both of the above oils and a sample several years old, the source of which was no longer known.

Canada Balsam Oil McKesson & Robbins

No. of Fraction	Temp. °C.	Wt. of Oil in Fraction	Total Weight	Percentage Weight	Sp. Gr. at 15°C.	Index of ref. at 15° C.
1	94.5	43.8	43.8	17.5%	.8616	1.4730
2	95.0	43.8	87.6	35.0	.8613	1.4740
3	95.5	44.3	131.9	52.7	.8613	1.4753
4	95.5	41.7	173.6	69.4	.8606	1.4764
5	96.0	26.6	200.2	80.0	.8590	1.4780
6	97.5	8.6	208.8	83.5	.8795	1.4836
7	98.5	4.3	213.1	85.2		1.4902

Canada Balsam Oil Milwaukee Drug Co.

(Sp.Gr., .8740 at 15°; index of ref., 1.4752 at 15°; Wt., 250 gm.)

No. of Fraction	Temp. °C.	Wt. of Turpen. in Fractions	Total Weight	Percentage Weight	Sp. Gr. at 15°C.	Index of ref. at 15° C.
1	94-94.9	48.2	48.2	19.3%	.856	1.4698
2	94.9-95	47.3	95.5	38.2	.859	1.4711
3	95-95	46.4	141.9	56.7	.860	1.4717
4	95-96	45.6	187.5	75.0	.860	1.4727
5	96-97	25.8	213.3	85.3	.862	1.4751
6	97-98	9.5	222.8	89.1	.865	1.4764
7	98-98.5	8.9	231.7	92.6	.882	1.4802

Canada Balsam Oil-Mixture of Milwaukee Drug Co.Oil, McKesson & Robbins and a Third Oil

Specific Gravity at 15° C.	0.8794
Index of Refraction at 15°C. ...	1.4794
Weight of Sample Taken	250 gm.

No. of Frac-tion	Temp. °C.	Wt. Of Oil in Fractions	Total Weight	Percent-age Weight	Sp. Gr. at 15°C.	Index of ref. at 15°C.
1	94.5-95	45.5	45.5	18.2%	.8550	1.4722
2	95.0-95.2	44.6	90.1	36.0	.8591	1.4735
3	95.2-95.3	44.7	134.8	54.0%	.8597	1.4742
4	95.3-96	43.0	177.8	71.0	.8602	1.4756
5	96 - 98	22.5	200.3	80.1	.8642	1.4781
6	98-98.4	9.6	209.9	84.0	.8742	1.4806
7	98.4-98.5	5.7	215.6	86.2		1.4825

The corresponding fractions from the three distillations were mixed and the combined fractions refractionated over direct heat with the aid of a two-bulb fractionating tube. The results are herewith tabulated.

From the preceeding table it becomes apparent that the steam fractionation with the Geer's column was fairly effective. The bulk of the mixed first fractions of the steam distillation passed over between five degrees, the bulk of the mixed second fractions between about six degrees, the bulk of the mixed third fractions between five degrees, the bulk of the mixed fourth fractions between six degrees.

Having determined the densities and angles of rotation of the fractions thus obtained, these fractions were again subjected to fractionation with the same column in order to ascertain whether a better resolution into a pinene and B-pinene fractions could be obtained.

Fractions Collected		Fractions from the Steam Distillation with Geer's Column Refractionated								Physical Constants	
No.	B.P.	I cc.	II cc.	III cc.	IV cc.	V cc.	VI cc.	VII cc.	Total cc.	Sp.Gr. 0/15°	In 100 mm. Tube
1	-158°	40.0	18.0						58.0	0.8603	-30.26°
2	158-159°	42.5	36.5	7.0					86.0	0.8632	-30.68°
3	159-160°	21.5	31.0	33.5	4.0				86.0	0.8625	-31.00°
4	160-161°	14.5	19.0	33.5	17.5				86.5	0.8623	-31.57°
5	161-162°	6.5	10.5	23.0	26.5	4.5	Started to		71.0	0.8611	-32.44°
6	162-163°	5.5	11.0	15.0	21.5	2.5	distill at		55.5	0.8612	-32.90°
7	163-164°	4.5	5.0	11.0	20.0	4.0	160°temp-		44.5	0.8614	-33.56°
8	164-165°	3.5	6.0	8.0	9.5	6.0	erature		33.0		
9	165-166°	---	4.0	6.0	11.0	12.0	rose to		33.0	0.8600	-35.50°
10	166-167°	---	4.0	4.0	7.0	13.0	169°,10		28.0	0.8602	-36.79°
11	167-168°	---	---	---	4.0	6.0	ccm of oil		10.0	0.8598	-38.00°
12	168-169°	---	---	---	6.0	5.0	were caught				
							7.5		18.5	0.8606	-38.20°
13	169-171°	---	---	---	5.5	9.0	3.0		17.5	0.8603	-40.35°
14	171-175°	---	---	---	3.0	12.0	4.0		19.0	0.8629	
15	175-178°	---	---	---	---	5.0	---		----	0.8674	

		Fractions Collected							
No.	B.P.	1	2	3	4	5	6	7	8
1	-158°	41.5	2.5	2.0	3.0				
2	158-159°	37.0	21.0	6.5	7.0	2.			
3	159-160°	14.5	27.0	13.0	8.0	5.5	2.5	2.5	2.0
4	160-161°	4.0	7.0	26.0	13.0	4.0	7.0	3.0	3.0
5	161-162°		2.0	12.0	17.0	9.5	7.5	4.0	3.5
6	162-163°			3.0	13.5	10.0	8.5	5.0	4.0
7	163-164°				3.5	6.5	8.5	7.0	4.0
8	164-165°					1.5	3.5	8.0	5.5
9	165-166°					1.5	3.5	5.5	4.0
10	166-167°						3.5	2.5	2.5
11	167-168°								
12	168-169°								
13	169-171°								
14	171-175°								
15	175-80								

								Physical Constants	
9	10	11	12	13	14	15	Total	Sp.Gr. at 15^{0}	In 100mm. tube
							49.0	0.8636	-30.00
							73.5	0.863	-30.29
							75.0	0.863	-30.75
3.0							70.0	0.863	-31.17
2.5	3.5						61.5	0.863	-31.91
1.5	2.5						48.0	0.864	-32.79
2.5	2.5	3.5					38.0	0.862	-33.42
2.5	3.0	2.0	3.0				29.0	0.864	-34.25
6.0	1.5	2.5	3.5				26.0	0.864	-35.87
6.5	4.0	2.0	2.5	4.5			28.0	0.861	-36.83
1.5	1.5	1.5	1.0	1.5			7.0	0.864	-38.03
1.0	2.0	2.0	2.5	2.5			10.0	0.862	-39.19
1.5	4.0	6.0	6.5	9.0			27.0	0.863	-40.08
					11.5		11.5	0.863	-44.82
						6.0	6.0		

In order to enable a more direct comparison of the fractions obtained in the two distillations with direct heat, the temperature at which the fractions distilled together with the densities and angles of rotation are herewith separately tabulated.

First Fractionation				Second Fractionation		
In 100mm. tube	Sp.Gr at 15°	Amount: c.c.	B.P.	Amount: c.c.	Sp.Gr. at 15°	In 100mm. tube
-30.26°	0.8603	58.0	-158°	49.0	0.863	-30.00°
-30.68°	0.8632	86.0	158-159°	73.5	0.863	-30.29°
-31.00°	0.8625	88.0	159-160°	75.0	0.863	-30.75°
-31.57°	0.8623	66.5	160-161°	70.0	0.863	-31.17°
-32.44°	0.8611	71.0	161-162°	61.5	0.863	-31.91°
-32.90°	0.8612	55.5	162-163°	48.0	0.864	-32.79°
-33.56°	0.8604	44.5	163-164°	38.0	0.862	-33.42°
		33.0	164-165°	29.0	0.864	-34.25°
-35.50°	0.8600	33.0	165-166°	26.0	0.864	-35.87°
-36.79°	0.8602	28.0	166-167°	28.0	0.861	-36.83°
-38.00°	0.8598	10.0	167-168°	7.0	0.864	-38.03°
-38.20°	0.8606	18.5	168-169°	10.0	0.862	-39.19°
-40.35°	0.8603	17.5	169-171°	27.0	0.863	-40.08°
	0.8629	19.0	171-175°	11.5	0.863	-44.82°
	0.8674		175-180°	6.0		

Volatile Oil from Oleoresin

The volatile oil of the oleoresin of Abies balsamea distilled from commercial samples of Canada balsam was examined by Unverdorben (1827), Flueckiger (1879), Dradwell (1891), Kressin (1892), Emmerich (1894), and by Tschirch and Bruening. (1900). The yield obtained by the several investigations is herewith tabulated.

Year	Investigator	Yield	Remarks
1825	Bonastre	18.6 p.c.	
1849	Wirzen	16.0 " "	
1879	Flueckiger	17-18" "	
1891	Flueckiger	24.0 ""	By distillation with water it is not easy to obtain more than 17 to 18% of essential oil. Pharmacographia 2d ed.p.613. Evidently not ascertained by steam distillation, but by "loss of weight determined with small amounts." Pharmacognosie, 3d ed.p.81. Comp. also Pharmacographia 2d ed. p. 613.
1891	Kradwell	19.5 p.c.	
1892	Kressin	22.0 ".".	
1900	Tschirch	24.0 " "	"Upon distillation of Canada balsam with water vapor, later with the addition of KOH." Arch. d. Pharm.,238, p.503.

Volatile Oil from Leaves

The only chemical investigation on record is that of C. G. Hunkel (1895) who had less than 100 grams of oil distilled from fresh twigs and cones at his disposal. Sp.Gr. 0.8881; (alpha)$_d$ -32.55°. He identified l-pinene

(nitrosochloride), borneol (m. p. 201-202°), and acetic acid (silver salt). The saponification of the oil revealed the presence of about 17.6 p. c. of l-bornyl acetate, in addition to l-pinene.

Composition

The earliest examination of the oil of Canada balsam that thows any light on its chemical composition appears to have been made by Flueckiger previous to 1879.(1) He pointed out that "by far the larger part boils at 167°" "has a sp. gr. of 0.863 and the power of rotating a ray of polarized light 5.60° to the left." He also makes the following statement, viz., that "The essential oil of Canada balsam, saturated with dry hydrochloric acid, does not yield a solid crystallizable compound; but this is easily obtained on addition of fuming nitric acid and gently heating, when the inside of the retort becomes covered by sublimed crystals of $C_{10}H_{16} + HCl$.

Kradwell(2) in 1891 found that the bulk of the oil distilled somewhat lower, viz., 90 p.c. between 160-163°, that fraction 160-161° had a sp. gr. of 0.857 at 20° and $(\text{alpha})_D$ -41.31°, and that it yielded a nitrosochloride, though in but small amount.

Emmerich(3) in 1894 not only verified the pre-

(1) Pharmacographia, 2d ed., p. 613.
(2) Proc. W. P. A., 12, p. 40.
(3) Am. Journ., Ph., 67, p. 135.

sence of pinene; but pointed out that the oil is apparently more complex than was at first supposed.

Resin

The resin from Canada balsam (McKesson and Robbins) was optically inactive in a twenty per cent solution of chloroform and gave a saponification value of 117.

The resin of Canada balsam from the Milwaukee Drug Co., gave an angle of rotation of +2.55° in a twenty per cent solution of chloroform. Its saponification value was 129.

Resin (McKesson & Robbins)

Resin Acid

(a) One hundred grams of resin were placed in a distilling flask and distilled under reduced pressure. A liquid distillate was obtained which did not become hard as did that from the Diggers pine resin. Attempts were made to crystallize out an acid from the distillate by means of alcohol and acetone. After standing for several weeks, no resin acid was noticed.

(b) To 125 grams of resin were added 750 grams of alcohol and allowed to stand for a few days in an Erlenmeyer flask. Not all of the resin could be dissolved. The insoluble portion was filtered off and heated with more alcohol in a reflux condenser. After heating one hour the alcoholic solution was poured into an evaporating

dish and allowed to remain several weeks. No resin acid crystallized out. The white insoluble portion was put into a bottle and marked "Material "A". The alcoholic solution of resin obtained previous to the first filtration was allowed to evaporate slowly. After standing three months, some crystals were observed. No attempt was made to separate them.

(c)

Some resin contained in a glass beaker and having a reddish appearance, was slowly dissolved in alcohol and allowed to evaporate in a large beaker. In a few weeks some pointed crystal clusters were observed upon the sides of the glass container and enclosed in the mother liquor. One of these clusters was mechanically removed and cautiously washed with alcohol. Its melting point was 145-149°. Observed with a magnifying lens, these crystals appeared to be triangular and transparent, in fact they closely resembled abietic acid in appearance.

The resin used in this case was from the Canada balsam obtained from the Milwaukee Drug Co. Its color was undoubtedly due to its having been heated above 140° when the original balsam was steam distilled.

No further work was done with the resin acid in attempting to separate it from the mother liquid.

RESIN ACID FROM OREGON BALSAM

Preliminary examination of an oleoresin from Douglas Fir

Acting upon the request of Acting Director Howard F. Weiss of the Forest Products Laboratory, Assistand Forest Ranger F. W. Stablman of the Santian National Forest at Detroit, Oregon, collected oleoresin, also twigs and cones of the "Douglas Fir". The identity of the latter was confirmed by Professor R. H. Denniston of the Botany Department of the University. The tree is also known to botanists by the synonym Pseudstsuga Douglasii (Lindl.) Can., and is commonly known as Douglas fir, red fir and Douglas spruce. As a possible source of the Oregon balsam, the Douglas fir and its oleoresin are of special interest to the phtochemist as well as to the pharmaceutical or analytical chemist.

Setting aside about 100 grams as reserve material and as specimen, the remaining oleoresin, about 336 grams, were subjected to steam distillation, thus resolving it into its volatile oil and resin, which, together with the original oleoresin, were examined as to their physical and chemical constants. The amount of material was too small for anything more than a preliminary survey.

The oleoresin was not clear like that obtained from Abies amabilis which was examined in 1904 and 1905

respectively by Rabak,(1) but had more of the emulsion-like appearance of ordinary turpentines, though liquid like the balsams. Attempts to separate water by dissolving the oleoresin in chloroform or by distilling with xylene, however, gave negative results.

The angle of rotation of a 20 p.c. alcoholic solution was determined in both a 100 mm. and in 200 mm. tube, and in each case the specific angle of rotation was computed to be $+1.48^\circ$.

1 gram of oleoresin, dissolved in 10 cc. of perfectly neutral alcohol and titrated with standardized alcoholic potassa, gave an acid value of 100.5. Heated for an hour on a water bath with an excess of alcoholic potassa, and titrated back, the saponification number was found to be 102.0. Duplicate determinations were made in both cases.

Of volatile oil, 51.5 grams or about 15 p.c. were obtained. Its specific gravity at 15°C. was 0.8705; its angle of rotation in a 100 mm. tube -40.46°, hence $(\text{alpha})_D = -46.47^\circ$. It had an agreeable terebinthinate, slightly camphoraceous odor when freshly distilled. 5 cc. yielded about 0.2 grams of a nitrosochloride, presumably pinene nitrosochloride. The small yield is in conformity with the high angle of rotation.

(1) Ph. Rev., 22, p. 293; also 23, p. 46.

The resin obtained upon steam distillation became hard upon standing. It was clear, but by no means of the light yellow color as that obtained from Abies amabilis.(1) To determine the angle of rotation, the resin was purified by evaporating the filtered chloroform solution. In a 20 p.c. alcoholic solution (d 0.845) it deviated the angle of polarized light 3.34° to the right, hence $(\text{alpha})_D = +19.6^{\circ}$.

The acid value of the resin was found to be 129, the saponification value 141. Duplicate determinations were made in both cases. The discrepancy between the two values as determined for the oleoresin and the resin can not be explained at present.

There are on record at least two earlier preliminary examinations of the volatile oil of the Douglas fir, the first by Blasdale in 1901,(2) the other by Frankforter in 1906.(3) The tabulation of a few of the data recorded may enable a better comparison.

	Blasdale	Frankforter	Beath
Yield of oil	abt. 9 p.c.	22 p.c.	15 p.c.
Sp. Gr.	0.8583 at 15°	0.8621 at 20°	0.8705 at 15°
Index of refraction	1.4754 at 15°	1.47299 at 20°	1.4710 at 20°
$(\text{alpha})_D$	-41.12°	-47.2°	-46.47°

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(1) Comp. l. c.
(2) Journ. Am. Chem. Soc., 23, p. 162.
(3) Ibidem, 28, p. 1467.

The variations in the physical constants are recorded are such as might be expected from an oil of the same species, although differences in the specific gravity are rather large. The variation in the yield, however, is more remarkable.

Since the Douglas fir has oleoresin-bearing pustules under the bark, the oleoresin from this species has been suggested as a possible source for the Oregon balsam of commerce. Its chemical examination, therefore, is of commercial as well as of phytochemical interest. Hence a further comparison of the properties of this oleoresin with those of the oleoresin of Abies amabilis, another possible source of Oregon balsam should give an added interest to the subject. For this purpose the data compiled by Rabak in the publications referred to above are utilized.

(See table next page)

Properties	Pseudotsuga taxifolia	Abies amabilis	Oregon Balsam, Commercial			
			"1903"	"1904"	"Portland"	"Dowzard"
			Oleoresin			
Sp.Gr.	----	0.969	1.01	0.985	0.988	0.993
(alpha)$_D$	+1.48	± 0°	+4°13'	+2°30'	+3°5'	-3°12'
Acid No.	100	44	116	103	114	
			Volatile Oil			
Yield	15 p.c.	40 p.c.	---	25 p.c.	---	---
Sp.Gr.	0.8705	0.852	0.857	0.882	---	0.8652
(alpha)$_D$	-46.47°	-12.17°	-37°46'	-34.37'	---	-37°34'
			Resin			
Alpha)$_D$	+19.6°	± 0°	---	---	---	---
Acid No.	129	70	153	---	---	---

A comparison of the above data justifies the conclusion that we are not much nearer to an understanding as to the botanical source of commercial Oregon Balsam than before, except possibly in so far that one more botanical possibility seems to have been eliminated. In addition to contants tabulated above, it should be pointed out that whereas oleoresin of Abies amabilis examined closely resembled the commercial oleoresin in color and general appearance, the oleoresin from Pseudotsuga taxifolia was milky in appearance and could scarcely have been substituted for either Oregon or Canada balsam.

Post Scriptum: Since writing the above the writer has received a communication from in which he states that the oleoresin from Pseudotsuga taxifolia,

under consideration, was obtained, not by puncturing the pustules, but by boring into the trunk. This may account for some of the discrepancies noted above.

BIBLIOGRAPHY

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Lescarbot, Marc. 1612

Histoiré de la Nouvelle-France

(The page references of the following extracts are those of the Nouvelle edition publice par Edwin Tross, Paris, 1866.)

p. 804.

"La terre de la Nouvelle-France est telle pour la plus part, de sablon gras, au dessoux dequel nous avons souvent tire de la terre argilleuse; et de cette terre le sieur de Poutrincourt fit faire quantitie de bricques, desquelles il batit des cheminees, et vn fourneau(2) a

"The soil of New France is chiefly coarse sand under which we have often found clayey soil; and of this clay the Sieur de Poutrincourt had a large quantity of bricks made of which he built chimneys and a furnace to melt(2)

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(1) The above quotations are given in full because less complete citations by Tschirch (Arch. d. Pharm., 238, p. 488) have been construed as evidence in favor of the idea that Canada Balsam is here necessarily implied. Tschirch, quotes the following"...fort souveraine a la Pharmacie. L'en ay baille a qulques Eglises de Paris pour encenser, laquelle a este trouvee fort bonne."

(2) Kalm, 1748-49, who does not even mention Canada balsam, calls attention to the "pitch kilns" which he passed at the Bay of St. Paul, where tar and pitch were obtained from the resinous roots of pines. He adds that they seemed not to understand the gathering of resin by cutting the bark of the pine trees as was done farther with Ph. Rev. 16, p. 264.

fondre la gomme de sapin.(3) Ie diray plus que de cette terre on peut faire les memes operations que de la terre que nous appellons Sigillee, ou du *Bolus Armenicus*, ainsi qu'en plusieurs occasions notre Apothicaire Maitre Loys Hebert tres-suffisant en son art, en a fait l'experience, par l' avis dudit Sieur de Poutrincourt; meme lors que le fils du Sieur Du Pont eut trois doigts emportez d'vn coup de mousquet creve au pais des Armouchiquois."

the gum of the fir(3) tree. I say further that this clay can be used in the same operations as the clay which we call bole or *Bolus Armenicus*. Thus on several occasions our apothecary, Maitre Loys Hebert, very efficient in his art, made the experiment, by the advise of the said Sieur de Poutrincourt; also when the son of Sieur du Pont lost three fingers by the discharge of a broken musket in the country of the Armouchiquois."

(3) "sapin" is also the French for spruce and pine, hence the reference may be to the semi-solid oleqresin of the pine. The solution of this "gum" in rape seed oil would seem to strengthen this supposition. Neither is it likely that the word "gum" would have been used for a liquid like Canada balsam. It certainly would not have been necessary to build a furnace for the purpose of melting Canada balsam."

"Et sur le propos de guerison il me souvient d'avoir oui dire au sieur de Poutrincourt qu'il avoit fait essay de la vertu la gomme des sapins(1) du Port Royal et de l'huile de navette sur vn garson fort mange de la mauvaise tigne, et qu'il en estoit gueri."

"In regard to healing, I remember having heard it said of sieur de Poutrincourt that he made an experiment to try the healing qualities by giving fir(1) gum of Port Royal and the oil of rape seed, to a boy who was afflicted with "mauvaise tigne" and that he was cured."

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p.820
"De bois exquis je n'y sache que le Cedre, et le Sasafras; mais des Sapins, et Pins, se pourra tirer vn bon proufit, parce qu'ils rendent de la gomme fort abondamment, et meurent bien souvent de trop de graisse. Cette gomme est belle comme la Terebentine de Venise, et fort souveraine a

p.820
Of choice wood I know only the cedar, and the sasafras; but of the firs and pines one could derive great profit, because they yield a great quantity of gum, and often die of too much oil. This gum is fine like the Venetian turpentine, and very valuable in pharmacy.

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(1) See foot note (3) page 36.

la Pharmacie. L'en ay baille a quelques Eglises de Paris pour encenser, laquelle a este trouvee fort bonne. On pourra davantage fournir de cendre cendres a la ville de Paris et autres lieux de France, lesquels d'orenavant s'en vont tout decouverts et sans bois."

I have given some to several churches in Paris to be used as incense(4) and it was found to be very good. One could also furnish ashes to other places in France, which henceforth are becoming bare and without trees"

Boucher, Pierre **1664**

Histoire veritable et naturelle.....de la Nouvelle France, vulgairement dite le Canada. (Reprinted in the Proc. and Trans. of the Royal Society of Canada, sec. ser., vol. II (1896), p. 116). The following extracts are taken from Chapter II: on the trees which grow in New France (p. 133 of the reprint).

"Ie commenceray par vn, qui est le plus vtile icy, que l'on nomme Pin, qui n'apporte pas de fruit comme ceux de l'Europe; il y en a de toutes groffeurs & grandeurs; ils viennent ordinairement de la hauteur de ciquante a soixante pieds,

"I shall begin with one, which is the most useful here, called the pine, which does not bear fruit like those of Europe. There are some of all sorts of sizes and thicknesses. They grow ordinarily to a height of

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(4) From Bouclier's account (1664) we learn that he burned "the gum" of the cedar like incense, not the "liquid gum" of the "buboes" of the fir and that this, has no other virtues at all "except balsam".

sans branches: l'on s'en sert pour faire de la planche qui est fort belle & bonne; & l'on dit que ces arbres seroient bien propre a faire des masts de Nauires. Il s'en trouue d'assez menu & haut pour cet effet: ces arbres font fort droits:il y a de grands Pays qui n'en portent point, mais les lieux ou ils naissent sront appellez Pinieres.	fifty to sixty feet without branches. It is used for making boards which are very fine and good, and it is said that these trees would be suitable to make into masts. There are plenty of them high and slender enough for that purpose. These trees are very straight. There are great sections where none grow, but the places where they grow are called pineries.
"Ces arbres rendent quantite de gomme; les Sauuages s'en seruent pour brayer leurs canots, & on s'en sert heureusement pour les playes, ou cette gomme est for souueraine.	These trees produce quantities of gum; The savages use it to coat their canoes, and it is successfully used in dressing wounds, for which this gum is excellent.
"Il croist aussi des Cedres, le bois en est fort tendre, il a la feuille platte, et le bois est quasi comme incorruptible: c'est pourquoy on s'en	"Cedars also grow there. The wood of these is very soft. It has a flat leaf, and the wood is almost indestructible. This is why

sert icy pour faire les clostures des jardins, & les poutres des caues: Il sent assez bon; mais d'ordinaire les arbres ne sot pas sains;cependant s'en trouve plusieurs gros qui pourroient servir a faire du meuble: il rend vne gomme, qui estant brulee, a vne tres bonne odeur comme de l'encent. Il ne fcache pas qu'elle aye d'autre qualite.

"Il y a des sapins comme en France;toute la difference que j'y trouve,c'est qu'a la l'ecorce, qui sont remplis d'vne certaine gomme liquide qui est aromatique, dont on se sert pour les playes comme de baumes, & n'a pas gueres moins de vertu, selon le raport de ceux qui ont fait l'experience: on en dit plusieurs autres

it is used here for garden fences and cellar beams, It smells quite good, but ordinarily the trees are not healthy: nevertheless some thick ones are found which might be used to make furniture. It yields a gum, which being burned has a very fine odor like incense. I do not know of its having any other quality.

"There are firs like in France; the only difference that I find is, that most of them get buboes on the bark which are filled with a certain liquid gum which is aromatic. This is used as balm for wounds, and has no other virtue at all,according to the report of those who have had experience with

choses, mais ie laisse cela aux Medecins."(1)

it. Other things are said of it, but I leave that to the physicians."(1)

"Die erste Erwahnung des in Amerika den Eingeborenen wohl seit langem schon bekannten und von ihnen gebrauchten Canadabalsam, geschah in einem Reisebericht von dem in Jahre 1606-1607 Canada bereisenden Marc Lescarbot(2) welcher denselben so schön wie venetianischen fand. Ebenso findet sich in Boucher's Histoire de la Nouvelle France(3) eine Stelle, in welcher mitgeteilt wird, dass es dort ebenfalls Tannen wie in Frankreich gabe; der unterschied bestände darin dass sich bei ersteren Drüsen in der Rinde befänden, welche von einem flussigen aromatischen Gummi erfüllt seien, welcher ein gutes Heilmittel für Wunden sei.

In Europa scheint dieser Balsam erst in 18. Jarhundert eingefuhrt worden zu sein. Noch nicht erwahnt finden wir

(1) From this account it becomes apparent that the oleoresin of the pines as well as that of the firs was used for "dressing wounds," and that the oleoresin of the cedar was used for incense purposes.

(2) Histoire de la Nouvelle France 1612. Neudruck Paris Ed. Tross III (1866), 805, 811, 820. "Fort souveraine en Pharmacie. J'en ay baille a qulques Eglises de Paris pour encenser laquelle a este fort bonne.

(3) Datiert 8. Oktober 1663, de la Ville des Trois Rivieres en la Nouvelle France.

ihn in Pomet's Werk(3) während er einige Jahre später von Lemery(4) als innerliches Heilmittel empfohlen wird. 1750 finden wir ihn in der Strassburger Taxe(5) und scheint er damals dort ein gangbarer Artikel der Pharmacie gewesen zu sein. Damals kostete nach der Taxe das Lot Canadabalsam 4 Schillinge. Merwürdig ist es, den Balsam hier zu treffen, da er um diese Zeit kaum in London allgemein bekannt war. Es is iedoch moglich, dass die Droge früher nach Frankreich kam, da Canada bis 1763 franzöisch war und erst später an England abgetreten wurde. Ebenso erwähnt ihn Lewis in seiner Hystory of the Materia Medica 1761 und nennt ihn, an elegant balsam, welcher von der Canada Fir erhalten wird. Er sagt, dass er zuweilen nach Europa unter dem Namen Canadabalsam gebracht wurde. Martius.(6)

(3) Pomet, Histoire generale des drouges 1694 und Histoire general des drouges 1735.

(4) Dictionnaire universel des Drouges simples. 3 me edit. Paris 1748, 2. Baume de Canada.

(5) Flückiger: Dokumente S. 92.

(6) Martius: Grundriss der Pharmakognosie 1832, S. 340.

giebt an, dass aus den Zweigen von Pinus canadensis (L) ein bereitet werde, idem man sie grob zerschnittem mit Gerste and Zukersirun garen lasse. Dasselve werde, Kalm gennant.

Terpentinöl aus Kanadabalsam.

Die erste Erwahnung des in Amerika den Eingeborenen wohl seit langem bekannten Kanadabalsams geschau in europaischen Reiseberivhten von dem in den Jahren 1606 bis 1607 Kanada bereisenden Marc Lescarbot.(8) Er bezeichnete den Balsam als gleichwertig mit dem venetianischen. In Europa scheint Kanadabalsam indessen erst im 18. Jahrhundret auf den Markt gelangt zu sein.(9)

Gyles, John 1736

Memoirs of old adventures, etc.

(Reprinted in S.G. Drake's Indian captivities,
New York, 1857.)

"After long traveling I felt very drowsy, and had thoughts of sitting down, which had I done, without doubt I had fallen in my final sleep, as my dear companion, Evans, had done before. My Indian companion, being better clothed, had left me long before. Again my spirits revived as much as if I had received the richest cordial. Some hours after sunset I reached the wigwam, and crawling in with my snowshoes on, the Indians cried out, "The capative is frozen to death!" They took off my pack, and the place where

(7) Archiv. d. Pharmacie. p. 487-588.

(8) M. Lescarbot, Histoire de la Nouvelle-France. 1612. Ed. Tross. Paris 1866. p. 805. 811, 820.

(9) Flückiger, Dokuments zur Geschichte der Pharmazie, S. 92. Gildemeister u. Hoffman. p. 105.

that lay against my back was the only one that was not frozen. They cut off my shoes, and stripped off the clouts from my feet, which were as void of feeling as any human fles could be. I had not sat long by the fire before the blood began to circulate, and my feet to my ankles turned black, and swelled with bloody blisters, and were inexpressibly painful. The Indians said one to another, "His feet will rot, and he will die." Yet I slept well at night. Soon after, the skin came off my feet from y ankles, whole, like a shoe, leaving my toes naked without a nail, and the ends of my great toes bones bare, which in a little time turned black, so that I was obliged to cut the first joint off with my knife. The Indians gave me rags to bind up my feet and advised me to apply fir balsam, but withal added that they believed it was not worth while to use means, for I should certainly die. But, by the use of my elboes, and a stick in each hand I shoved myself along as I sat upon the ground over the snow from one tree to another, till I got some balsam. This I burned in a clam-shell till it was of a consistence like salve, which I applied to my feet and ankles, and, by the divine blessing, within a week I could go about upon my heels with my staff. And, through God's goodness, we had provisions enough, so that we did not remove under ten or fiteen days. Then the Indians made two little hoops, something in the form of a snow whoe, and sewing them to my feet, I was able to follow them in their tracks on my heels, from place to place, though sometimes half leg deep in snow and water, which gave me the most acute pain imaginable, but I must walk or die. Yet within a year my feet were entirely well; and the nails came on my great toes, so that a very critical eye could scarcely perceive any part missing, or that they had been frozen at all."

,In as much as the interest in the above passage lies as much in the report of the antiseptic and therapeutic effect of the "fir balsam" is in the mere reference thereto, the paragraph is herewith quote in extenso. The page reference (pp. 87-88) is the above mentioned reprint.

Lewis, Wm. 1761

An Experimental History of the Materia
Medica.
(The following extracts are taken from a copy kindly
loaned for this purpose by the Lloyd Library.)

"1. *Abies Pharm. Paris*.

"2. *Picea*: *Abies picea Pharm*. *Paris*.

"3. *Abies Canadensis Pharm*. *Paris*. *Abies minor pectinatis foliis*, *virginiana*, *conis parvis subrotundis Plukenet*. Virginia or Canada fir; with roundish-pointed leaves, sometimes cloven, standing like the teeth of a comb in two rows on each side the branches, and variegated underneath with a double line of whitish dots.(1)

"4. *Balsamea*: *Abietis taxi foliis species odore balsami gildeadensis Raii suppl*. Balm-of-gilead fir; so called from the fragrant smell of the leaves when rubbed. The leaves are roundish-pointed, and slightly cloven, nearly like those of the silver fir: the cones are long and pointed, and stand erect.

These foreign firs, now naturalized to our own climate, promise to be superior, for medicinal uses, to the two preceding; their resinous matter being of a finer and more grateful kind. From the Canada fir is extracted, in America, by wounding it during the summer heats, an elegant balsam, which is sometimes brought into Europe under the name of balsamum Canadense. The balm-of-gilead fir has a more agreeable fragrance, approaching to that of the celebrated balsam from which it receives its name. A

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(1) Linnaens, *species plantorium*, 1002

valuable resin exudes from the cones, in considerable quantity; and resins nearly of the same kind may be extracted by spirit of wine, both from the cones and from the leaves."

Coxe, J. R. 1806

The American Dispensatory.

Pinus.

Monoecia Adelphia-- Nat. ord. Coniferae.

+ + +

Pinus Balsamea. Hemlock-fir.

Resina. Ed. Balsamum Canadense. L. D.

Balsam of Canada (p. 512)

+ + +

Terebinthina.

Turpentines have different appelations, chiefly according to the country from which they are procured.

Balsam of Canada, from the Pinus balsamea et Canadensis.

Resina. Ed. Balsamum Canadense. L. D.

+ + +

None of these are properly balsams, which term is now used to express those oily resinous substances only which contain benzoic acid.

+ + +

Each species has some peculiarities. The Canadian is recorded the best, and next to it the Chian. (p. 514).

U. S. P. 1820

Terebinthina Canadensis Pinus balsamea. W.IV.504.

Canada balsam Balsamum. The balsam.

Unverdorben, O. 1827.

Ueber die Harze. Poggend. Annal., 11, p. 27.

The author includes Canada balsam (p. 39) in his investigations of the resins and states merely that it gave the same results as did Venice turpentine (p. 34). However, he did not test the former for succinic acid which he found in the latter. The constituents found in Venice turpentine are:

1.) A readily volatile oil.
2.) A difficultly volatile oil.
3.) A large amount of colophony or pininic acid.
4.) An indifferent resin.
5.) A small amount of succinic acid.
6.) A small amount of bitter extractive.
7.) A trace of resin insoluble in petroleum.

U. S. P. (N. Y.) 1830.

Terebinthina Canadensis Pinus Balsamea.

Canada Balsam

Similar in its general properties to the other turpentines, but more fragrant.

U. S. P. (Phila.) 1831.

Terebinthina Canadensis. Pinus balsamea.W.IV.504.

Canada Balsam Succus. The juice.

Cailliot, A. 1830

Sus les terebenthines des sapins redresse a cone.

Journ. de Pharm., 16, p. 436.

The author reports that he has included the "terebenthina du Canada" in his investigations, but his report on this particular turpentine is restricted to the following footnote (p. 441). "Toutes propnites que j'ai reconnues pur la premiere fois dans la sous-resine de l'abies balsama (Journ. Comple. des Scien medic., t. 22). Neither Flueckiger, who does mention this (Pharmacognosie, p. 81) nor Tschirch who concludes that Caillot had obtained a crystalline "Abietine" have seen this original (Arch. d. Pharm., 238, p. 488.

U. S. P. 1842

Terebinthina Canadensis. Canada Turpentine.

Syn. Canada balsam. Balsam of fir.

The juice of Abies balsama. (Lindly Flor.Med.).

U. S. P. 1864

Terebinthina Canadensis. Canada Turpentine.

Syn. Balsam of Fir.

The juice of Abies balsamea (Lindley, Flor. Med.).

Peck, C. H. 1872

The Balsam Fir.

Twenty-first Annual Report on the N. Y. State Natl. Museum p. 21. 1880. New Remedies, p. 267; Ph. Journ., 40, p.333; Proc. A. Ph. A. p.

An account of the natural history of the tree with only a casual reference to the "Canada balsam".

U. S. P. 1873

Terebinthina Canadensis. Canada Turpentine.

Syn. Balsam of Fir.

The liquid oleoresin obtained from Abies balsamea. (Lindley, Flor. Med.)

Morel, J. 1877

The turpentines and resinous products of the Coniferae. II Canada Balsam.

Pharm. Journn., 37, p. 21.; Proc. A. Ph. A.,26, p. 314.

The author gives a general account of the plant (synonyms, description) and of the oleoresin (synonyms, extraction, characters, composition) and makes a comparison between the results (physical constants and composition) obtained by Bonastre, Flückiger and Wirzen.

Hitschson, Ed. 1877

Beitraege zur Chemie der wichtigesen Gummiharze, Harze und Balsame.

Archiv. der Pharmacie 211, p. 152.

The author outlines several reactions distinguishing Canada balsam from turpentine. (p. 159).

I. Alcohol and ether-alcohol dissolve only a portion.
II. Ether solution is rendered turbid alcohol.
III. Lead Acetate produces a insoluble in the cold.
IV. Iron chloride gains shortly after mixing a turbidity which disappears upon heating, also upon the addition of ether.
V. Sodium carbonate solution does not combine at room temperatures.
VI. Chloral produces a yellow color turning to violet red upon standing.

Saunders, Wm. **1877.**

Canada Balsam.

Proc. Am. Ph. Assoc., 25, p. 337.
Pharm. Journ., 37, p. 813.

The committee on the Drug Market in its report for 1877 gives Mr. W. E. Brimet's (Chemist of) account of the methods employed in securing the oleoresin, and what precautions are necessary to insure the best yield from year to year.

Flückiger and Hanbury. **1879.**

Terebinthina Canadensis.

Pharmacographia, 2nd. ed., p. 612.

A general account, particularly of historical value.

Kradwell, G. V. **1891.**

Proc. W. P. A., 12, p. 37
Proc. A. Ph. A., p.

Terebinthina canadensis, with a review of the different varieties of turpentine.

The author identified l-pinene in the oil by means of its nitrosochloride and received indictions of the presence of a camphor-like body. Contrary to Flückiger's statement, he obtained a crystalline substance from the resin, persumably an acid.

Kressin, L. H. **1892.**

Notes on Pinene.
Proc. W. P. A., 13, p. 66.
Proc. A. Ph. A., p.

The oil from Canada balsam, yield 22 p. c., was carefully fractionated. An attempt to prepare an optically active pinene nitrosochloride gave negative results. (Comp. also Emmerich 1894.)

Emmerich, H. 1894.

Volatile Oil from Canada Balsam.

Amer. Journ. Pharmacy, 67, p. 135.
Proc. A. Ph. A., 43, p. 853.

The author reports the results of a somewhat detailed study of the fractions left by Kressin (1892) not only verifying the presence of pinene, but showing that the oil is more complex than at first supposed.

Humkel, C. G. 1895.

Volatile Oil of Abies Balsamea.

Am. Jour. Pharm., 1895, 9.
Am. Ph., A., 43, p. 1027.

The author gives an account of oil obtained from distilling twigs and cones from the fir tree. In addition to laevogyrate pinene, laevogyrate bornyl acetate was identified.

Dietrich, E. 1897.

Balsamum Canadense.

Dezemium der Helfenberger Annalen. p. 27.

The author records the following results, obtained from an analysis of Canada balsam:

Acid number: 84.00 - 86.80.
Iodine number: 180.42 - 236.07.
Chloroform)
Acetic ether)(Soluble
Benzol)
Ether: Nearly soluble.
Turpentine oil

CS_2: Almost soluble.

Alcohol of 90%: 90.90 to 93.58% soluble.
Petroleum ether: 83.46 to 92.73% soluble.

Dietze, F. 1897.

Suedd. Apt. Ztg., p.
Jahresber. d. Pharm., 32, p.42 (1)

In connection with three commercial samples of Canada balsam the author determined the following chemical constants.

	I.	II.	III.
Acid value (direct) (1)	84.89	85.93	84.40
Ester value	4.54	9.83	9.00
Saponification value, hot	89.43	95.76	93.40

The acid value was determined according to Kremel's method, the saponification value by the "usual method."

Gregor and Bamberger 1898.

Oesterredchische Chemiker Zeitung p. (2)

The methoxyl for Canada balsam was found to be 0.

Tschirch, A. and Bruening, G. 1900.

Uber den Harz balsam von Abies Canadensis
(Canada Balsam).

Arch. d. Pharm., 238, 487.
Proc. A. Ph. A., 49, p. 744.

The authors approximate the percentages of resin acids, volatile oil and indifferent resin present in the oleoresins of resin acids. They isolated four:

Canadinic acid, $C_{19}H_{30}O_2$ (amorphous)

Canadolic acid, $C_{19}H_{28}O_2$ (cryst. abt. 0.3 p.c.)

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(1) Comp. also Dieterich-Salter, Analysis of resins, balsams and gum-resins, p. 61.

(2) Information obtained through K. Dieterich, Analysis of resins, balsams and gum-resins, p. 6.

Tschirch, A. and Bruening, G. (con) **1900**

Canadinolic acid, $C_{19}H_{30}O_2$ (amorphous)
(alpha)
Canadinolic acid, $C_{19}H_{30}O_2$ (amorphous)
(beta)

There is also a resin, $C_{21}H_{40}O$, and the Volatile Oil.

Blasdale, W. C. **1901.**

On Heptane from Coniferous Trees.

Jour. Amer. Chem. Soc., 23, p. 162.

The author found the oleoresin of Pseudotsuga taxifolia to yield an oil of the following nature:

Specific gravity at 15°	0.8583
Refractive index at 15°	1.4754
$(alpha)_D$	-41.12°

Iodine absorption high.
Yield of oil about 9 per cent.

Rabak, F. **1904.**

Oregon balsam.

Pharm. Rev., 22, p. 293.
Proc. A. Ph. A., 53, p. 687.

The author reviews the earlier literature on the subject and records the physical and chemical constants of these commercial samples of "Oregon balsam" and of their components, the volatile oil and resin. He also finds l-pinene in the volatile oil.

Rabak, F. **1905.**

Oleoresin of Abies Amabilis.

Pharm., Rev., 23, p. 46.
Proc. A. Ph. A., 53, p. 685.

The author has made a study of the physical and chemical constants of the oleoresin and its components, the volatile oil and resin, and has ascertained the presence of l-pinene in the oil.

Frankforter, G. B. 1906.

The Pitch and the Terpenes of the Norway Pine and the Douglas Fir.

Jour. Am. Chem. Soc., 28, p. 1467.

The author reviews the yield of fir "pitch" from different grades of wood and outlines the physical and chemical constants of the oleoresin and volatile oil.

Wood rich in "pitch" gives 42.4% oleoresin.

Wood poor in "pitch" gives 11.6% oleoresin.

Oleoresin of Douglas fir:

Specific gravity at 20°	0.9821
Refractive Index at 20°	1.51785
(alpha)$_D$	-8.82°

Volatile Oil of Douglas Fir:

	Steam Distilled	Destructive Distilled
Specific Gravity at 20°	0.8621	0.8662
Boiling point	153.5°-154°	157°-160°
Refractive Index	1.47299	1.47246
(alpha)$_D$	-47.2°	-29.40°
Yield = 22%		

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